

State of charge monitoring for vanadium redox flow batteries by the transmission spectra of V(IV)/V(V) electrolytes

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Received: 13 March 2012 / Accepted: 18 August 2012 / Published online: 1 September 2012
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Abstract A method is presented for monitoring the state of charge (SOC) of vanadium redox flow batteries (VRBs) by the transmission spectrum of the positive electrolyte [V(IV)/V(V)]. We use the transmission spectrum rather than the absorption spectrum for better signal noise ratio. In order to solve the complicated relations between the spectrum and the SOC of the VRB, the entire shape of the spectrum is utilized instead of the data at one wavelength. We experimentally demonstrate that SOC from 0 to 100 % can be monitored by comparing the transmission spectra of the positive electrolytes [V(IV)/V(V)] with the database, which is previously built by detecting standard samples. The method has potential ability to monitor the level of imbalances of the VRB, which is important for rebalancing the electrolyte and restoring the capacity loss of a VRB.

Keywords Vanadium redox flow battery ·
State of charge · Spectrophotometric ·
Transmission spectra · Electrolyte

1 Introduction

The vanadium redox flow battery (VRB) is a type of rechargeable flow battery that employs vanadium ions in different oxidation states to store chemical potential energy

[1, 2]. The VRB has many benefits including no cross-contamination, indefinite life of the vanadium electrolyte, and long cycle life compared with other technologies [3–5]. However, a number of side reactions, such as air oxidation of the V(II) ions, gassing side reactions, the differential transfer of vanadium ions and water across the membrane could lead to an imbalance between the positive and the negative electrolytes, and a subsequent loss of capacity over extended charge–discharge cycling [6, 7]. In order to rebalance the electrolytes and thereby restore the loss of capacity, a suitable state of charge (SOC) monitoring method is needed to detect the level of the imbalances.

Some SOC monitoring methods, such as the open-circuit voltage (OCV) [8], the potentiometric titration, and the chromatography, have been widely used. However, these methods have their limitations. The SOC of the imbalanced system is difficult to detect by OCV method. The potentiometric titration and the chromatography have complex steps, and therefore are not suitable for real-time monitoring of the SOC during the VRB operation. Skyllas-Kazacos et al. [6, 7] proposed a method to monitor the SOC by combining the conductivity and the spectrophotometric studies of the electrolytes. However, the conductivity of the electrolytes is affected not only by the SOC, but also by many other factors such as the temperature and the concentration of the electrolyte. The spectrophotometry is an applicable way for real-time monitoring of the SOC. Nevertheless, the total concentration of the vanadium ions for practical use in a VRB is too high (the typical value is close to 2 M). Thus, the absorbance of the electrolyte does not obey the Beer's law, and the signal to noise ratio (SNR) is very low. Furthermore, as there are interferences between the vanadium ions with different valences, the total absorbance cannot be calculated by the combination of the absorbance of each ion. In Skyllas-Kazacos et al.'s

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study [7], only the absorbance at certain wavelengths (e.g., 750 nm) of the negative electrolyte [V(II) and V(III)] can be used for the SOC monitoring. To our knowledge, no one has reported monitoring the SOC of the VRB by use of the spectrum of the positive electrolyte [V(IV)/V(V)].

Our team has studied VRB for many years [5, 9–12] and also has experiences in optical detections [13–15]. In this paper, we develop a new method for monitoring the SOC of the VRB based on detecting the transmission spectrum of the positive electrolyte [V(IV)/V(V)]. For a better SNR, the transmission spectrum is used as the detection result rather than the absorption spectrum. Moreover, to solve the complicated relations between the spectrum and the SOC of the VRB, the entire shape of the spectrum is utilized instead of the data at one wavelength.

2 Materials and methods

2.1 Electrolyte preparation

First, 100 % V(IV) solution with certain vanadium concentration (e.g., 1.9 M) is prepared by dissolving vanadyl sulfate in H_2SO_4 supporting electrolyte with certain H_2SO_4 concentration (e.g., 2.5 M). Second, 100 % V(V) solution is prepared by the electrolysis of 100 % V(IV) solution. Finally, the V(IV)/V(V) solutions of compositions corresponding to different SOC are prepared by mixing 100 % V(V) solution and 100 % V(IV) solution with the same vanadium and H_2SO_4 concentrations in different ratios. For instance, the electrolyte of 100 % V(IV) corresponds the SOC of 0 %, the electrolyte of 99 % V(IV) and 1 % V(V) corresponds the SOC of 1 %, and so on.

Twenty-one kinds of electrolytes corresponding to different SOC from 0 to 100 % (with 1.9 M total vanadium

and 2.5 M H_2SO_4) are prepared. Samples of these electrolytes are loaded into cuvettes of 1 mm thickness, and their appearances are shown in Fig. 1. It is shown from Fig. 1 that the pure V(IV) (SOC 0 %) electrolyte is light blue and the pure V(V) (SOC 100 %) electrolyte is yellow. When a little V(V) is mixed into the pure V(IV) electrolyte, the solution quickly becomes darker (SOC 1–5 %), which indicates the increase of the absorption. Similar phenomenon happens when a little V(IV) is mixed into the pure V(V) electrolyte (SOC 99–95 %). Thus in a wide range of SOC (10–90 %), the electrolytes have very high absorption and are black to naked eyes. This phenomenon is probably due to the interferences between V(V) and V(IV) vanadium ions in such a high concentration, making the traditional spectrophotometric method difficult to detect the SOC of the positive electrolyte.

2.2 System setup

A home-made transmission spectrum analytical system is built, and the schematic is shown in Fig. 2. Light from a white light point source (A, CDHC-Optics GCI 0601, 150 W halogen lamp) is collimated by an achromatic convex lens (B, CDHC-Optics GCL 010651, $f = 40$ mm) and then is split into two beams by a beam splitter (C, Thorlabs BS013). One beam is focused by another achromatic convex lens (D, same model as B) and collected by a photo detector (E, Texas Instruments OPT101). The output of the detector is digitized by the data acquisition card of a personal computer (I). The other beam passes a customized absorption cell (F), which allows the electrolyte (F2) to flow between two glass windows (F1) and form a 1 mm thick uniform layer. The light passing through the absorption cell goes into the entrance slit (G1) of a grating spectrometer (G, SpectralPro 150, Acton research). The light leaving the spectrometer is collected

Fig. 1 Samples of the positive electrolytes [V(IV)/V(V)] with different sates of charge (SOCs) in 1 mm cuvettes. The total vanadium concentration is 1.9 M and the H_2SO_4 concentration is 2.5 M

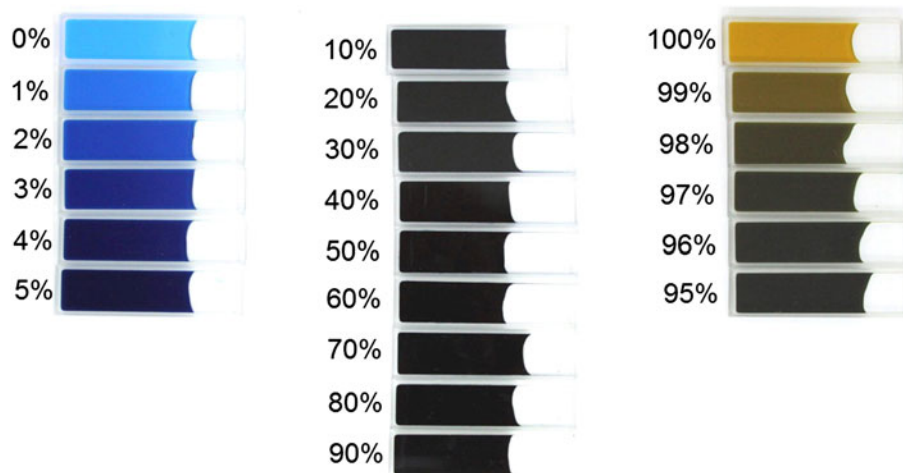
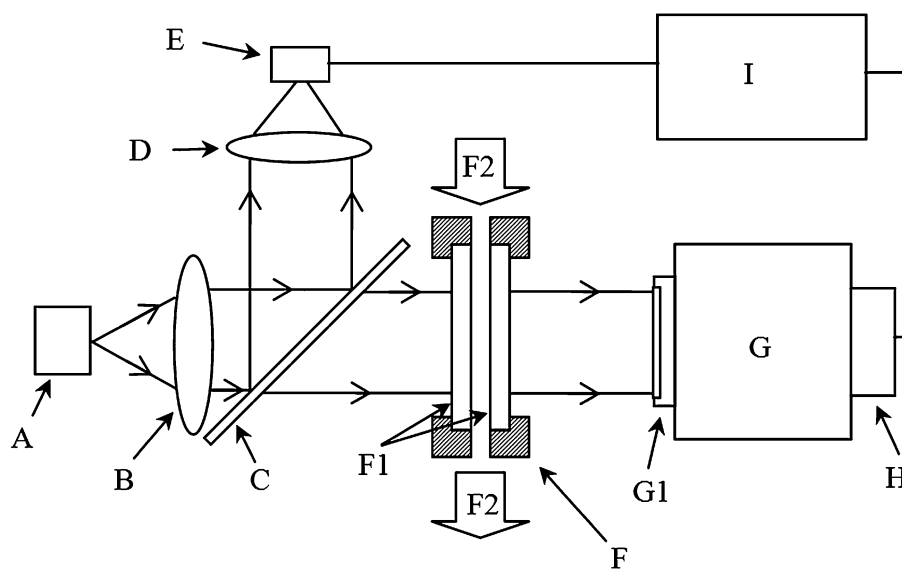


Fig. 2 The schematic of the transmission spectrum analytical system. A white light point source, B achromatic convex lens, C beam splitter, D achromatic convex lens, E detector, F absorption cell (F1 glass window, F2 electrolyte), G grating spectrometer (G1 entrance slit), H CCD camera, I PC



with a CCD camera (H, Q-imaging RETIGA EXi 1394) placed on the focal plane, and the images acquired by the CCD are transmitted to the personal computer (I).

Together with the fluctuation of the light source intensity detected by the photo detector (E), the spectrum information of the electrolyte contained in an image captured by the CCD (H) could give us the normalized transmission spectrum of the 1 mm thick electrolyte sample layer.

3 Results and discussion

3.1 Transmission spectra of V(IV)/V(V) electrolytes with different SOC

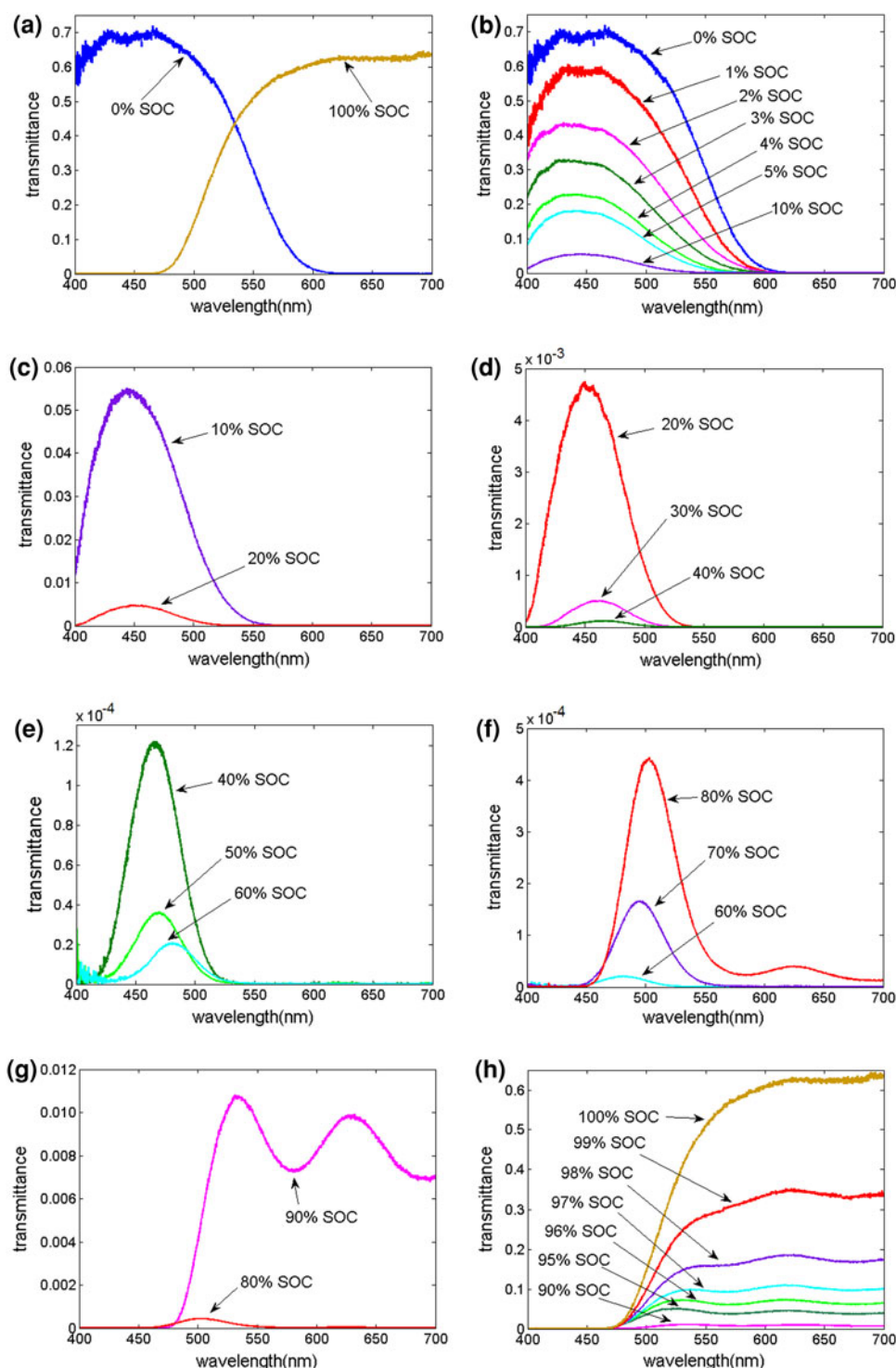
The V(IV)/V(V) electrolytes corresponding to different SOC are prepared (with 1.9 M total vanadium and 2.5 M H_2SO_4 , see details in Sect. 2.1), and flow through the 1 mm absorption cell of our transmission spectrum analytical system (F in Fig. 2 of Sect. 2.2). The system measures the normalized transmission spectra of these electrolytes, which are shown in Fig. 3a–h. It is shown in Fig. 3a that the pure V(IV) (0 % SOC) and the pure V(V) (100 % SOC) have similar transmittance intensities (0.6–0.7) but different spectral ranges. Hence they appear light blue and yellow, respectively, in Fig. 1. As the SOC rises from 0 to 10 % (Fig. 3b), the intensity of the peak near 450 nm in the transmittance spectrum quickly reduces from 0.6 to around 0.06. This agrees with the color changing from light blue to dark blue and black in Fig. 1. As increasing of the SOC continues (Fig. 3c–e), the intensity of the peak further drops to 5×10^{-3} (20 % SOC), 5×10^{-4} (30 % SOC), 1.2×10^{-4} (40 % SOC), and 4×10^{-5} (50 % SOC). The peak intensity reaches the

minimum of approximately 2×10^{-5} when the SOC is 60 % (Fig. 3e). Meanwhile, the transmission peak moves slightly to the long-wavelength direction and reaches 470 nm when the SOC increases to 60 % (Fig. 3e). The intensity of the transmission peak begins to increase when the SOC increases above 60 %, and keeps moving to the long-wavelength direction (Fig. 3f). Furthermore, another peak appears at longer wavelength (80 % SOC in Fig. 3f). The SOC keeps increasing to 90 %, there are apparently two peaks in the visible range and their intensity quickly rise to around 0.01 (Fig. 3g). Since then, as the SOC increases, the intensity of the transmittance continue to rise and the peaks gradually disappear, until the final shape of the spectrum becomes that of the pure V(V) (Fig. 3h).

From the transmission spectra of the V(IV)/V(V) electrolytes with different SOC described in Fig. 3, it can be seen that at the same total vanadium concentration of 1.9 M and the H_2SO_4 concentration of 2.5 M, the transmission spectra of the electrolytes change dramatically with different SOC: the shape changes and the intensity of the peak varies from 0.6 down to 2×10^{-5} then back to 0.6. This abnormal phenomenon is probably due to the interference between V(V) and V(IV) vanadium ions in such a high concentration. This is the main reason why traditional spectrophotometric methods have difficulties for real-time analysis of the positive electrolyte in a VRB [7]. In this study, we optimize our home-made transmission analytical system in many areas (light source, absorption cell, detector etc.). So with our system, we could detect the spectral variation process of the V(IV)/V(V) electrolytes at practical concentration during the change of SOC for the first time as we know.

In addition, the transmission intensity of the V(IV)/V(V) electrolyte shows the minimum value in the whole

Fig. 3 Normalized transmission spectra of electrolytes with the SOC from 0 to 100 %. The total vanadium concentration is 1.9 M and the H_2SO_4 concentration is 2.5 M



visible range when the ratio of the V(IV) and V(V) is 3:2 (60 % SOC). Thus it is reasonable to speculate that the V(IV) and V(V) ions form a special coordination structure in such ratio and concentration. This will be further studied in our future works.

3.2 Method to monitor the SOC by the transmission spectra

Based on the detection results in Sect. 3.1, we propose a method for monitoring the SOC of the VRB by the

transmission spectra of the V(IV)/V(V) electrolytes, as shown in Fig. 4. First, the normalized transmittance spectrum of the positive electrolyte in a VRB with unknown SOC is detected by our spectrum analytical system. Then, the resulting spectrum (Fig. 4a) is compared with all the spectra in our transmittance spectra database (Fig. 4b), which have been built by previously detections of standard electrolytes. Algorithms such as correlation analysis are used to determine the most similar spectrum in the database compared with the sample. Finally, we look into the database to find the parameters (such as SOC) of this most similar electrolyte. Then the parameters (such as SOC) of the sample are considered the same.

In order to testify the feasibility of the method, 5 different types of V(IV)/V(V) electrolytes with unknown SOC are sampled from an operating VRB, whose initial electrolytes are produced from the electrolysis of an electrolyte solution with 1.9 M VOSO_4 and 2.5 M H_2SO_4 . We used both our spectral method and the potentiometric titration method to test the SOC of these 5 V(IV)/V(V) electrolytes, and the results are shown in Fig. 5. We can conclude from Fig. 5 that the SOC determined by two methods are in good agreement. The difference of these two results are due to the incomplete database, which only has the spectral data with SOC of 10 % interval.

3.3 Extension of the spectra database

In Sect. 3.2, our database only has the spectra of the V(IV)/V(V) electrolytes at the same total vanadium concentration (1.9 M) and the same H_2SO_4 concentration (2.5 M). In order to expand the database, V(IV)/V(V) electrolytes corresponding to different SOC and with different total vanadium

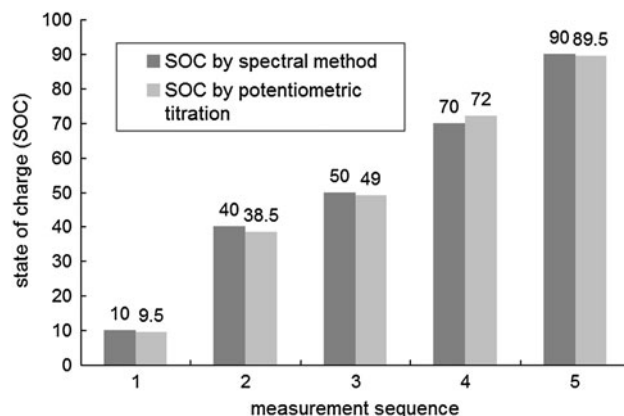


Fig. 5 The SOC of 5 samples measured by our spectral method and the potentiometric titration method. The samples are from operating VRB, whose initial electrolytes are produced from the electrolysis of an electrolyte solution with 1.9 M VOSO_4 and 2.5 M H_2SO_4

concentration and different H_2SO_4 concentration are produced with the method introduced in Sect. 2.1. All the transmission spectra of these electrolytes are detected by our system, and saved into the database. In order to illustrate the impact of the total vanadium concentration and the H_2SO_4 concentration on the spectra of the V(IV)/V(V) electrolytes, some of the results are shown in Figs. 6, 7.

Figure 6a–d show the impact of the total vanadium concentration (from 1.9 to 1.4 M) on the spectra of the V(IV)/V(V) electrolytes (with 2.5 M H_2SO_4) corresponding to SOC of 0, 10, 50, and 100 %, respectively. We can see from Fig. 6 that with the total vanadium concentration decreases, the transmission spectrum of the electrolyte increases, with different increasing rates depend on the SOC of the electrolytes. The electrolyte corresponding to SOC of 50 % increases the fastest (Fig. 6c). Note that the intensity differences of the

Fig. 4 Method for monitoring the SOC of the VRB by the transmission spectrum of the V(IV)/V(V) electrolyte

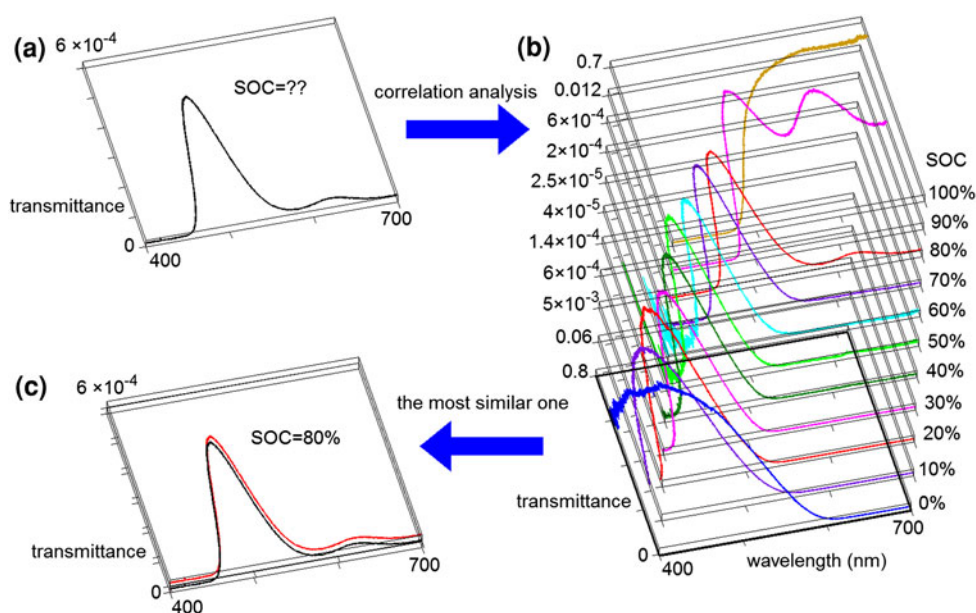


Fig. 6 a–d The impact of the total vanadium concentration (from 1.9 to 1.4 M) on the spectra of the V(IV)/V(V) electrolytes (with 2.5 M H_2SO_4) corresponding to SOC of 0, 10, 50, and 100 %, respectively. The squared area in **c** are enlarged and shown in the upper right corner of **c**

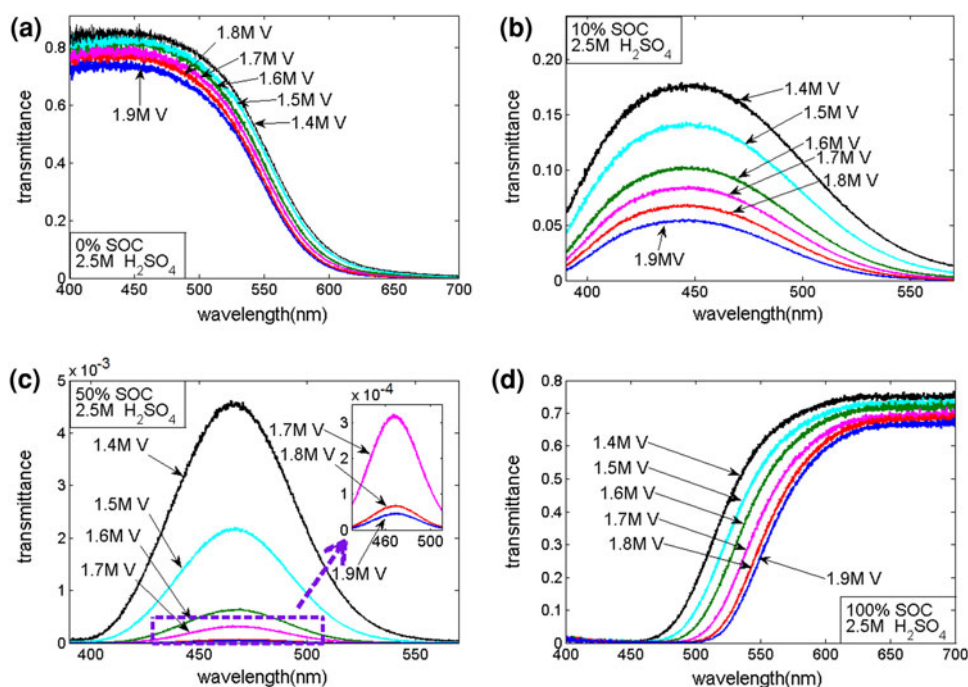
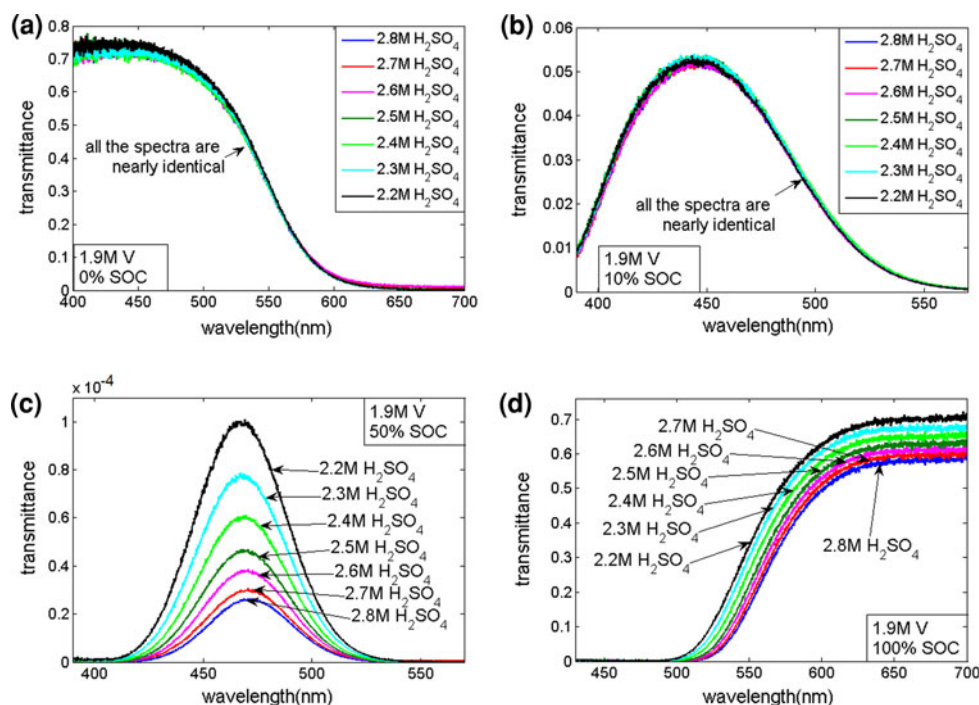


Fig. 7 a–d The impact of the H_2SO_4 concentration (from 2.8 to 2.2 M) on the spectra of the V(IV)/V(V) electrolytes (with 1.9 M total vanadium) corresponding to SOC of 0, 10, 50, and 100 %, respectively



spectra in Fig. 6c are too big that we enlarge the squared area and show it in the upper right corner of Fig. 6c.

Figure 7a–d show the impact of the H_2SO_4 concentration (from 2.8 to 2.2 M) on the spectra of the V(IV)/V(V) electrolytes (with 1.9 M total vanadium) corresponding to SOC of 0, 10, 50, and 100 %, respectively. It can be seen from Fig. 7 that with the H_2SO_4 concentration

decreases, the spectra of the electrolytes corresponding to SOC of 0 and 10 % [pure and 90 % V(IV)] remain the same; but the spectra of the electrolytes corresponding to SOC of 50 and 100 % [50 % and pure V(V)] increases, with different increasing rate. These results indicate that the H_2SO_4 concentration does not affect the spectra of V(IV), but do affect the spectra of V(V).

From the results in Figs. 6, 7, we can conclude that there are complicated relations between the spectra of the V(IV)/V(V) electrolytes and the parameters such as SOC, the total vanadium concentration, and the H_2SO_4 concentration. This increases the difficulty of the traditional spectrophotometric methods for analyzing of the positive electrolyte in a VRB.

In order to decide the imbalance of a VRB, both the SOC of the positive and negative electrolytes must be known. However, the negative electrolyte in a VRB is easily oxidized in air, hence is not suitable to prepare and analyze, and only can be measured real-time in an operating VRB. So in this paper we did not detect the negative electrolyte of the VRB. In our further studies, both the positive and the negative electrolytes will be analyzed real-time during the charge–discharge process. With the database containing the spectra of both the negative and the positive electrolytes, our system will have the ability to determine the level of the imbalances in a VRB. That is useful for rebalancing the electrolytes and thereby restoring the capacity loss of a VRB system.

4 Conclusion

A method for monitoring the state of charge (SOC) of the VRB by the transmission spectrum of the positive electrolyte [V(IV)/V(V)] is present. We use the transmission spectrum as the detection result rather than the absorption spectrum for better signal noise ratio (SNR). In order to solve the complicated relations between the spectrum and the SOC of the VRB, the entire shape of the spectrum is utilized instead of the data at one wavelength. We experimentally demonstrate that SOC from 0 to 100 % of the positive electrolytes [V(IV)/V(V)] can be monitored by comparing the transmission spectra with the database, which is previously built by detecting standard samples. With the expanded database to be built in our further work,

our method has potential ability to monitor the level of imbalances in a VRB. This will be helpful to rebalance the electrolytes and restore the capacity loss of a VRB system.

Acknowledgments This research was made possible with the financial support from the National Natural Science Foundation of China (20973099), the Basic Research Program of Shenzhen City (JC201005310703A, JC201005310712A, JC200903180530A, CXB201005250040A), and Shenzhen Science Fund for Distinguished Young Scholars (2011).

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